Quantum and classical mode softening near the charge-density-wave/superconductor transition of Cu_xTiSe_2: Raman spectroscopic studies

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Temperature- and x-dependent Raman scattering studies of the charge density wave (CDW) amplitude modes in Cu_xTiSe_2 show that the amplitude mode frequency ω_o exhibits identical power-law scaling with the reduced temperature, T/T_{CDW}, and the reduced Cu content, x/x_c, i.e., $\omega_o \sim (1 - p)^{0.15}$ for $p = T/T_{CDW}$ or x/x_c, suggesting that mode softening is independent of the control parameter used to approach the CDW transition. We provide evidence that x-dependent mode softening in Cu_xTiSe_2 is caused by the reduction of the electron-phonon coupling constant λ due to expansion of the lattice, and that x-dependent 'quantum' ($T \sim 0$) mode softening reveals a quantum critical point within the superconductor phase of Cu_xTiSe_2.

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One of the most important current goals of condensed matter physics research involves elucidating the competition between diverse and exotic phases in strongly correlated matter, such as antiferromagnetism and superconductivity (SC) in the high T_c cuprates,[1] heavy fermions,[2] and cobaltates,[3] and charge density wave (CDW) order and SC in materials such as Na_xTaS_2.[4] Recently, Morosan *et al.* discovered an interesting new material exhibiting a competition between CDW order and SC: copper intercalated 1*T*-$TiSe_2$, i.e., Cu_xTiSe_2.[5] 1*T*-$TiSe_2$ is a semimetal or small-gap semiconductor in the normal state,[6, 7, 8, 9] which develops a commensurate CDW with a $2a_o \times 2a_o \times 2c_o$ superlattice structure at temperatures below a second-order phase transition at $T_{CDW} \sim 200$ K.[6, 10] Increasing Cu intercalation in $TiSe_2$ (increasing x in Cu_xTiSe_2) results in (i) an expansion of the a- and c-axis lattice parameters,[5] (ii) increased electronic density of states near the L point,[7, 8] (iii) a suppression of the CDW transition temperature,[5] and (iv) the emergence near $x = 0.04$ of a SC phase having a maximum T_c of 4.15 K at $x = 0.08$.[5]

The Cu_xTiSe_2 system provides an ideal opportunity to investigate the microscopic details of quantum ($T \sim 0$) phase transitions between CDW order and SC. It is of particular interest to clarify the nature of the "soft mode" in CDW/SC transitions: the behavior of the soft mode - i.e., the phonon mode whose eigenvector mimics the CDW lattice distortion, and hence whose frequency tends towards zero at the second-order phase transition - is one of the most fundamental and well-studied phenomena associated with classical (thermally driven) displacive phase transitions;[11] on the other hand, soft mode behavior associated with quantum phase transitions is not well understood. In this investigation, we use Raman scattering to study the temperature- and doping-dependent evolution of the CDW 'amplitude' modes in Cu_xTiSe_2. The CDW amplitude mode [12] - which is associated with collective transverse fluctuations of the CDW order parameter - offers detailed information regarding the evolution and stability of the CDW state and the CDW soft mode. In this study, we show that the amplitude mode frequency in Cu_xTiSe_2 exhibits identical power-law scaling with the reduced temperature, T/T_{CDW}, and the reduced Cu content, x/x_c, indicating that mode softening in Cu_xTiSe_2 is independent of the control parameter used to approach the CDW transition. Further, we show that 'quantum' ($T \sim 0$) softening of the CDW amplitude mode is consistent with a quantum critical point hidden in the superconductor phase of Cu_xTiSe_2, suggesting a possible connection between quantum criticality and superconductivity.

Raman scattering measurements were performed on high quality single-crystal and pressed-pellet samples of Cu_xTiSe_2 for $x = 0$, 0.01, 0.02, 0.03, 0.04, 0.05, and 0.06, which were grown and characterized as described previously.[5, 13] Fig. 1(a) shows the $T = 6$ K Raman spectra of Cu_xTiSe_2 for various Cu concentrations (x). The $T = 6$ K Raman spectrum of $TiSe_2$ (top spectrum in Fig. 1) exhibits several spectroscopic features that have been reported previously,[14, 15] including a Raman-active $\mathbf{k} = 0$ phonon mode near 137 cm^{-1} that shows little change in energy ($\sim 0.7\%$), and only a slight increase in linewidth, with increasing x. Also apparent in Fig. 1(a) are several modes that appear below the CDW transition, including an A_{1g}-symmetry amplitude mode near 118 cm^{-1}, which arises from fluctuations of the CDW amplitude that preserve the ground state $2\times2\times2$ CDW structure, and an E_g-symmetry amplitude mode near 79 cm^{-1}.[14, 15] These CDW amplitude modes are associated with the soft zone boundary TA phonon at the

L-point,[14, 15] which is folded to the zone center when the unit cell is doubled below T_{CDW}.[16]

Fig. 2 summarizes the A_{1g} amplitude mode frequency (squares) and linewidth (circles) in Cu_xTiSe_2 as functions of (a) Cu concentration, x (for T = 6 K) and (b) temperature (for x = 0). The A_{1g} amplitude mode frequency and linewidth data were extracted from Lorentzian fits to the data, as illustrated for some select spectra in Fig. 1. Because the A_{1g} amplitude mode (dashed lines, Fig. 1) is in most cases well-separated from, or much broader and stronger than, nearby optical modes (dotted lines, Fig. 1), estimated errors in the amplitude mode frequency obtained in this manner were $\leq 1\%$. Fig. 2(b) illustrates that the A_{1g} amplitude mode of Cu_xTiSe_2 exhibits temperature-dependent soft mode behavior typical of amplitude modes observed in other CDW systems,[17,18] including: (i) a temperature-dependence (filled squares, Fig. 2(b)) given by the power law form $\omega_o(T) \sim (1 - T/T_{CDW})^{\beta}$ with $\beta \sim 0.15$ (solid line, Fig. 2(b)), (ii) a weakening of the amplitude mode intensity as the CDW lattice loses coherence as $T \rightarrow T_{CDW}$, and (iii) a dramatic increase in linewidth with increasing temperature (filled circles, Fig. 2(b)); the latter mainly reflects overdamping of the amplitude mode due to an increase in CDW fluctuations, as it is in substantial excess of the broadening expected from anharmonic (i.e., two-phonon) contributions (dashed line, Fig. 2(b)). The anomalous temperature dependence of the 118 cm^{-1} A_{1g} amplitude mode in Cu_xTiSe_2 confirms that its eigenvector couples strongly to the lattice distortion responsible for the CDW transition at T_{CDW}, and thus mimics the collapse of the soft mode and the CDW gap as $T \rightarrow T_{CDW}$.

Significantly, Fig. 1(a) shows that both the 79 cm^{-1} E_g and 118 cm^{-1} A_{1g} amplitude modes in Cu_xTiSe_2 also exhibit x-dependent mode softening that has nearly identical characteristics to temperature-dependent mode softening in Cu_xTiSe_2. For example, Fig. 2(a) shows that the A_{1g} amplitude mode softens by $\sim$18% between x = 0 and x = 0.05 at T = 6 K (solid squares), and exhibits a 400% increase in linewidth between x = 0 and x = 0.04 at T = 6 K (solid circles). Note that the dramatic x-dependent increase in the T = 6 K amplitude mode linewidths (filled circles, Fig. 2(a)) cannot be attributed to the effects of disorder (e.g., inhomogeneous broadening caused by Cu substitution), as there is not a comparably large increase in the other phonon linewidths with increasing x. Rather, x-dependent damping of the CDW amplitude modes in Cu_xTiSe_2 reflects a dramatic enhancement of CDW fluctuations - and a loss of CDW coherence - with increasing x. A microscopic analysis of the nature and origin of x-dependent mode softening in Cu_xTiSe_2 (see Fig. 2(a)) can be made using Rice and collaborators mean-field result for the frequency of a CDW amplitude mode,[12]

$$\omega_o = 1.4\lambda^{1/2}\tilde{\omega}t^{1/2}, \qquad (1)$$

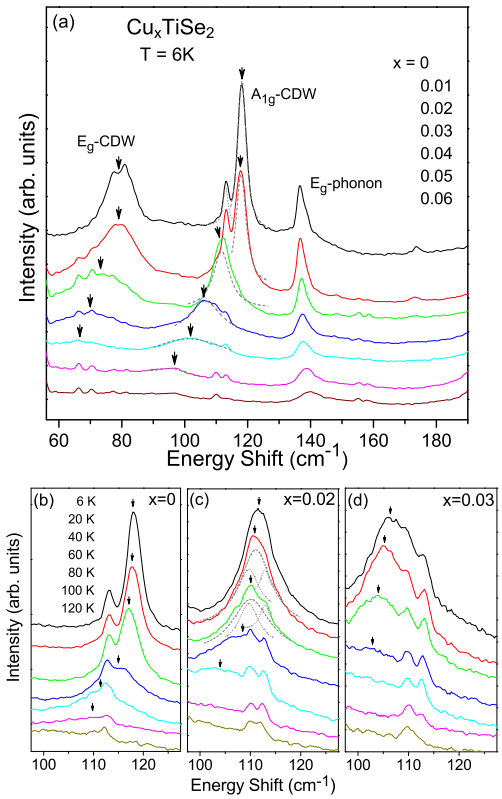

FIG. 1: (a). Doping (x) dependence of the Raman spectrum of Cu_xTiSe_2 at T = 6 K, illustrating the E_g- and A_{1g}-symmetry CDW 'amplitude' modes (arrows) as a function of x. (b)-(d) Temperature dependence of the A_{1g}-symmetry CDW mode spectra at (b) x = 0, (c) x = 0.02, and (d) x = 0.03 in Cu_xTiSe_2. The spectra have been offset for clarity, and the vertical scales in (c) and (d) are respectively 3× and 4× the vertical scale in (b). Also shown are example Lorentzian fits to the A_{1g} amplitude mode (dashed) and nearby optical modes (dotted).

which has been successfully applied to the analysis of CDW soft mode behavior in other dichalcogenides.[17] In Eq. 1, $\tilde{\omega}$ is the unscreened (high temperature) phonon frequency, $t = (T_{CDW}\text{-}T)/T_{CDW}$ is the reduced temperature, and $\lambda = N(0)g^2(0)/\tilde{\omega}$ is the electron-phonon coupling constant associated with the CDW, where g(0) is the electron-phonon coupling matrix element between the soft mode phonon and the electronic states at the Fermi surface involved in the CDW transition, and N(0) is the joint density of states of the electrons and holes involved in the CDW transition.[17] Note that the unscreened frequency $\tilde{\omega}$ in Eq. (1) is not expected to have a significant doping dependence between x = 0 and x = 0.06 in Cu_xTiSe_2, which is supported by the fact that the optical phonon frequencies exhibit a negligible change with x (e.g., see 137 cm^{-1} mode in Fig. 1). Conse-

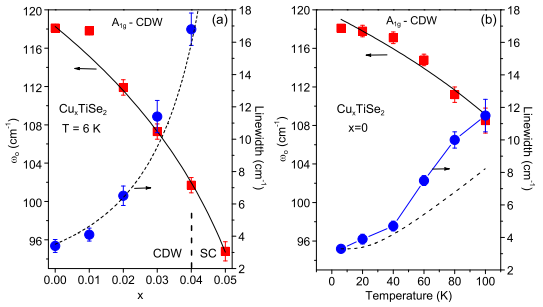

FIG. 2: (a). Summary of the T = 6 K A_{1g}-symmetry CDW mode frequency (ω_o) vs. x (filled squares) and the T = 6 K A_{1g}-symmetry CDW mode linewidth (FWHM) vs. x (filled circles) for Cu_xTiSe_2. The solid line is a fit to the doping dependence of the T = 6 K frequency data using $\omega_o/\omega_o(0)=(1 - x/x_c)^\beta$ with $\beta \sim 0.15$ and $x_c \sim 0.07$, and the dashed line is a fit to $\Gamma \sim (x_c - x)^{-2}$ with $x_c \sim 0.07$. (b). Summary of the x = 0 A_{1g}-symmetry CDW mode frequency (ω_o) vs. temperature (filled squares) and the x = 0 A_{1g}-symmetry CDW mode linewidth (FWHM) vs. temperature (filled circles) for $TiSe_2$. The solid line is a fit to the frequency data with $\omega_o/\omega_o(0) = (1 - T/T_{CDW})^\beta$ with $\beta \sim 0.15$. The dashed line illustrates the contribution to the linewidth expected from two-phonon damping. The estimated errors from the Lorentzian fits are $\leq$ 1% for the frequency data and $\leq$ 8% for the linewidth data. The linewidth data includes a ~ 0.5 cm^{-1} contribution from instrumental broadening that has been accounted for in fits to the data.

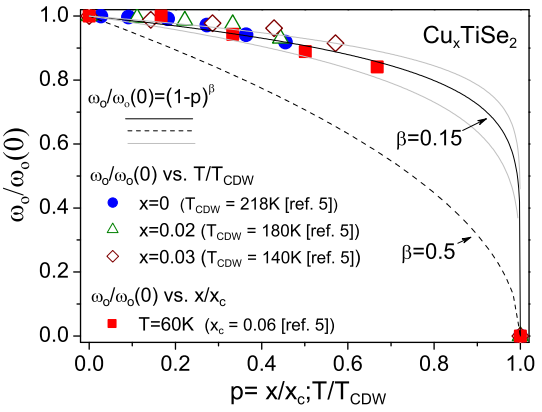

FIG. 3: Plots of $\omega_o/\omega_o(0)$ vs. x/x_c for T = 60 K (x_c = 0.06 [5]) (filled squares), and $\omega_o/\omega_o(0)$ vs. T/T_{CDW} for x = 0 (T_{CDW} = 218 K [5]) (filled circles), x = 0.02 (T_{CDW} = 180 K [5]) (open triangles), and (iv) x = 0.03 (T_{CDW} = 140 K [5]) (open diamonds). The top dashed line in Fig. 2(c) shows that all these data sets collapse onto the same curve given by $\omega_o/\omega_o(0) = (1 - p)^\beta$, where $\beta = 0.15$ and $p = x/x_c$ or T/T_{CDW}. The gray lines provide an estimate of the uncertainty in β by comparing fits with $\beta = 0.2$ (bottom) and $\beta = 0.10$ (top). The estimated errors for the frequency data ($\leq$ 1%) are roughly given by the symbol sizes.

quently, Eq. 1 suggests that the x-dependent softening of the A_{1g} amplitude mode in Cu_xTiSe_2 is associated with a substantial reduction in the electron-phonon coupling constant λ with doping in Cu_xTiSe_2. One possible source of this reduction is a decrease in the density of electrons/holes participating in the CDW transition between x = 0 and x = 0.05 in Cu_xTiSe_2, N(0). Indeed, Morosan *et al.* observed a ~50% decrease in the size of the magnetic susceptibility drop below T_{CDW} between x = 0 and x = 0.05 in Cu_xTiSe_2, indicating that fewer electronic states are gapped at the CDW transition with increasing x.[5] Importantly, however, this reduction in N(0) is not likely associated with a loss of Fermi surface nesting with increasing x, because ARPES studies of Cu_xTiSe_2 have shown that nesting actually increases with doping.[7] Another possibility is that the primary effect of Cu intercalation on the CDW phase is caused by the linear expansion of the a-axis parameter with Cu intercalation in Cu_xTiSe_2,[5] which leads to a reduction in λ by expanding the Ti-Se bond length primarily responsible for the CDW instability in 1T-$TiSe_2$.[6, 16, 19] Notably, this alternative is consistent with Castro Neto's proposal that the layered dichalcogenides have a critical lattice spacing above which CDW order is suppressed.[20]

Remarkably, Fig. 3 shows that, in spite of the different microscopic effects of doping (x) and temperature on the lattice, x-dependent and thermal mode softening in Cu_xTiSe_2 exhibit essentially identical scaling behavior. In particular, Fig. 3 compares the following data sets: (i) the normalized A_{1g} amplitude mode frequency $\omega_o/\omega_o(0)$ vs. the reduced doping x/x_c for T = 60 K (using x_c = 0.06 from ref. 5) (filled squares); and (ii) the normalized A_{1g} amplitude mode frequency $\omega_o/\omega_o(0)$ vs. the reduced temperature T/T_{CDW} for x = 0 (using T_{CDW} = 218 K from ref. 5) (filled circles), x = 0.02 (T_{CDW}=180K [5]) (open triangles), and x = 0.03 (T_{CDW}=140K [5]) (open diamonds) (similar results are obtained from the E_g amplitude mode frequency). The solid line in Fig. 3 shows that all these data sets collapse onto the same curve given by $\omega_o/\omega_o(0) = (1 - p)^\beta$, with $p = x/x_c$ or T/T_{CDW} and $\beta \sim 0.15$. An estimated uncertainty of $\Delta\beta = \pm 0.05$ in the "best fit" value of $\beta \sim 0.15$ is suggested by the gray lines in Fig. 3, which show the functional form $\omega_o/\omega_o(0) = (1 - p)^\beta$ for both $\beta = 0.20$ (bottom gray line) and $\beta = 0.10$ (top gray line).

Two key points should be made regarding Fig. 3: First, although we cannot measure the amplitude mode frequency with temperature (doping) all the way to the critical point T_{CDW} (x_c), for reasons described above, we can nevertheless extract a reliable value for the scaling parameter β from fits to these data in Fig. 3 because we know the values of T_{CDW} (for all x) and x_c (at T

= 60 K) from ref. 5. Second, we note that the scaling parameter $\beta \sim 0.15$ obtained from our amplitude mode data is substantially smaller than the value of 1/2 suggested by the mean-field model of Eq. 1.[12] However, the scaling parameter of $\beta \sim 0.15$ in Cu_xTiSe_2 is consistent with the critical exponent for the order parameter in the 2D three-state Potts model, $\beta = 0.133$;[21] this model—which has the same symmetry as the free energy used by McMillan for the layered dichalcogenides[14]—is appropriate for Cu_xTiSe_2 because of the 3 commensurate CDWs in this material.[6, 11]

The 'universal' scaling of the Cu_xTiSe_2 amplitude mode as functions of both T/T_{CDW} and x/x_c in Fig. 3 emphasizes that x-dependent mode softening - like more conventional thermal mode softening - is associated with a critical point at x_c that drives both critical softening behavior ($\omega_o \rightarrow 0$) and overdamping of the amplitude mode as $x \rightarrow x_c$. Indeed, the x-dependent amplitude mode softening data between $0 < T \leq 100$ K, which are summarized in Fig. 4, suggest the presence of a CDW phase boundary line $x_c(T)$ in Cu_xTiSe_2 that extends from the phase boundary line established by Morosan *et al.*[5] down to a quantum (T∼0) critical point. To obtain quantitative estimates of $x_c(T)$ in Cu_xTiSe_2 from our data, the ω_o vs x curves in Fig. 4 were fit using the same functional form as that used to fit the x-dependent data at T = 60 K in Fig. 3, i.e., $\omega_o(x) = \omega_o(0)(1 - x/x_c)^\beta$ with $\beta \sim 0.15$, where $\omega_o(0)$ is the x = 0 value of the A_{1g} amplitude mode frequency at a particular temperature. Note that the quantities contributing to the prefactor, $\omega_o(0)$, should not have a significant x-dependence: the reduced temperature factor in Eq. (1) varies less than 5% between x = 0 and x = 0.06, and the unscreened frequency $\tilde{\omega}$ in Eq. (1) is not expected to have a significant doping dependence in Cu_xTiSe_2 for reasons described above. Additionally, in obtaining estimates of $x_c(T)$ from our data, we assume that the scaling parameter $\beta \sim 0.15$ obtained from fits to the T = 60 K data in Fig. 3 doesn't vary significantly for the ω_o vs x curves at the other temperatures shown in Fig. 4 - this assumption is justified by the wide range of ω_o vs. T and ω_o vs. x curves that scale according the power law form $\omega_o \sim (1 - p)^{0.15}$ in Fig. 3 (p = T/T_{CDW} or x/x_c), and by theoretical predictions for the critical exponent expected for the order parameter in a 2D system with a three-fold degenerate ground state, $\beta = 0.133$.[11, 21]. Thus, the resulting fits of the data in Fig. 4 (solid lines) have only $x_c(T)$ as an unconstrained parameter. The estimates of $T(x_c)$ obtained from the fits in Fig. 4 are represented by the filled circles in the inset of Fig. 4; also shown for comparison are previous measurements of $T(x_c)$ (open circles) by Morosan *et al.*[5] The reasonableness of our $T(x_c)$ estimates is supported by two self-consistency checks: First, our estimates of $x_c(T)$ provide good fits of the x-dependent A_{1g} amplitude mode linewidths using the functional form, $\Gamma(T) \sim (x_c(T) - x)^{-\gamma}$, as illustrated by the dashed line in Fig. 2(a) for $\gamma \sim 2$; and second, our estimated value for x_c(T = 80 K) overlaps with the known phase boundary line from Morosan *et al.*[5]

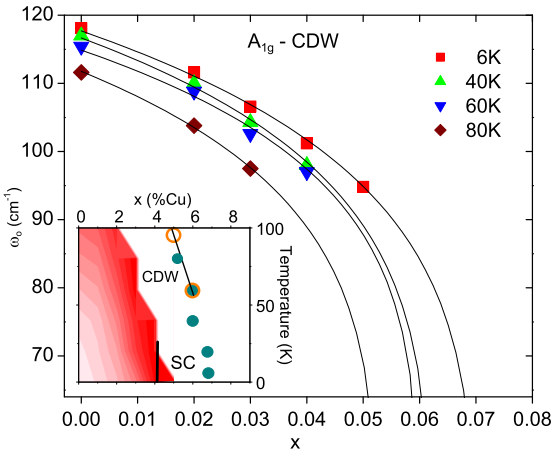

FIG. 4: Summary of the A_{1g} amplitude mode frequency ω_o) vs. x for different temperatures. The solid lines are fits using $\omega_o/\omega_o(0) = (1 - x/x_c(T))^\beta$, w/ β = 0.15-0.16. (inset) Estimated values of $T(x_c)$ from the fits (filled circles); T_{CDW} data from ref. 5 (open circles) is shown for comparison. The inset also shows a contour plot of the temperature and x-dependent linewidth Γ data, which ranges from light red ($\Gamma \sim 3$ cm^{-1}) to dark red ($\Gamma \sim 17$ cm^{-1}). The solid line denotes the superconductor (SC) phase boundary line. The estimated errors for the frequency data ($\leq 1\%$) and $T(x_c)$ values are roughly given by the symbol sizes.

The values of $T(x_c)$ estimated from our x-dependent mode softening results in Fig. 4 are consistent with a low temperature CDW phase boundary in Cu_xTiSe_2 that extends from the phase boundary line measured by Morosan *et al.*[5] down to a quantum critical point at roughly $x_c(T = 0) \sim 0.07$. This suggests that SC and fluctuating CDW order coexist in the doping range x ∼ 0.04 - 0.07 of Cu_xTiSe_2. Furthermore, this result suggests that the Cu_xTiSe_2 phase diagram is consistent with the T vs. lattice parameter phase diagram plotted by Castro Neto for the layered dichalcogenides, in which there are two quantum critical points as a function of increasing lattice parameter: superconductivity (SC) and CDW order coexist above the lower of the two critical lattice parameters, while SC is present, but CDW order is not, above the higher of the two critical lattice parameters.[20] We note, however, that because the amplitude mode becomes overdamped and unobservable very close to the transition region - due to the breakdown of long-range CDW order and zone-folding [17, 18] - we cannot rule out the possibility that other effects, e.g., disorder from Cu intercalation, may lead to different quantum critical behavior (i.e., for T ∼ 0 and near x ∼ 0.07) than that implied

by the x-dependent scaling behavior we observe up to x = 0.05 in Fig. 4. Consequently, it would be useful to study the putative transition region $x_c(T = 0) \sim 0.07$ with methods more sensitive to short-range, fluctuating CDW order, such as inelastic x-ray or neutron scattering. It is nevertheless interesting that the value of the quantum critical point $x_c(T = 0) \sim 0.07$ estimated from our x-dependent mode softening data is close to the peak in $T_c(x)$, suggesting a possible connection between SC and the presence of fluctuating CDW order in Cu_xTiSe_2. Indeed, the inset of Fig. 4 also shows a contour plot of the temperature and x-dependent A_{1g} amplitude mode linewidth, Γ, which ranges from light red ($\Gamma \sim 3$ cm^{-1}) to dark red ($\Gamma \sim 17$ cm^{-1}), illustrating the dramatic increase of CDW fluctuations as the phase boundary is approached with increasing x and/or temperature. Another indirect connection between quantum critical behavior and the expansion of the lattice in Cu_xTiSe_2 is also suggested by the fact that pressure studies of $1T$-$TiSe_2$ [14] don't show evidence for pressure-induced T$\sim$0 softening of the A_{1g} amplitude mode that would indicate the presence of a quantum critical point; this suggests that pressure (lattice compression) and Cu intercalation (lattice expansion) have fundamentally different effects on the quantum phases of $1T$-$TiSe_2$.

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